Supporting information for
"Unraveling the Wacker Process Mechanisms"
John A. Keith, Robert J. Nielsen, Jonas Oxgaard, William A. Goddard, III

(1) Calculation Details:

We report relative free energies as differences between the calculated absolute free energy, G, of two species. For species involving transition metals, we define G as:

$$G_{mol} = E_{gas} + E_{solv} + ZPE + H_{vib298} + 3*RT - T*S_{vib298} + RT*\ln(24.5)$$

where RT = .592 kcal/mol at 298 K. See below for additional discussion of energy terms.

For H_2O:

$$G_{H2O} = -47962.6 \text{ kcal/mol.}$$

This value is obtained by taking our gas phase absolute free energy, $G_{H2O} = E_{gas} + ZPE + H_{vib,H2O} + 3*RT + pV - T*S_{tot,H2O}$, -47960.6 kcal/mol and adding -2.05 kcal/mol (the free energy of vaporization for H_2O).[1]

For Cl^-:

$$(3) \qquad G_{Cl-} = -288908.8 \text{ kcal/mol.}$$

This value is obtained by taking our gas phase absolute free energy, $E_{gas} + 3/2*RT + pV - T*S_{tot,Cl-}$ ($S_{tot,Cl-}$ = 36.7 cal/mol*K)[2] and adding -74.6 kcal/mol (the free energy of solvation for Cl^-.)[3]

For H^+:

$$(4) \qquad G_{H+} = -265.5 \text{ kcal/mol}$$

Reasoning for why we use this energy rather than the full free energy of a solvated proton, i.e., $G_{H+(gas)} + G_{H+(solv)}$ = (-6.3 kcal/mol)[2] – (264.0 kcal/mol)[3a] = -270.3 kcal/mol, is explained below in section 3-b.

(2) Discussion of Energy Terms:
E_{gas} and E_{solv} are calculated with computational techniques outlined below. ZPE, H_{vib}, S_{vib}, and S_{tot} contributions are obtained from vibrational frequency calculations with thermodynamic calculations at 298K unless otherwise noted.

Thermal contributions are added to account for translations (3/2*RT in all species) and rotations (3/2*RT in all species but Cl^-). We only use S_{vib} contributions in molecular species involving transition metals since, in our experience, including S_{trans} and S_{rot} terms increases errors in associative ligand exchange barriers involving Pd and Pt complexes. All gas phase calculations include an additional term pV = RT = .592 kcal/mol. All calculations involving calculated values of E_{solv} include a free-energy correction to account for adjusting from standard states in gas to aqueous solution: RT*ln(24.5) = 1.9 kcal/mol.

All calculations were carried out with Jaguar 6.5[4] using the hybrid-density functional theory, B3LYP.[5] Molecular geometries and vibrational frequencies were obtained from solvent-relaxed geometries obtained

[1] Donald D. Wagman, William H. Evans, Vivian B. Parker, Richard H. Schumm, Iva Halow, Sylvia M. Bailey, Kenneth L. Churney, and Ralph L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, Vol. 11, Suppl. 2 (1982).
[2] Chase, M.W., Jr., NIST-JANAF Themochemical Tables, Fourth Edition, *J. Phys. Chem. Ref. Data,* Monograph 9, **1998**, 1-1951.
[3] (a) Tissandier, M.D.; Cowen, K.A.; Feng, W.Y.; Gundlach, E.; Cohen, M.H.; Earhart, A.D.; Coe, J.V.; Tuttle, T.R.; *J. Phys. Chem. A.* **1998**, *102*, 7787. (b) Palascak, M. W.; Shields, G. C. *J. Phys. Chem. A* **2004**, *108*, 3692; (c) Camaioni, D. M.; Schwerdtfeger, C. A. *J. Phys. Chem. A* **2005**, *109*, 10795.
[4] Jaguar 6.5, Schrodinger, LLC, New York, NY, 2005.

with Jaguar's Poisson-Boltzmann implicit solvation program ($\varepsilon = 80.37$ and $r_{solvent} = 1.400$Å)[6] and with an overall double-zeta quality electronic core potential containing 18 explicit electrons, LACVP**[7] on Pd, and the 6-31G** basis set on all other atoms. From these "solvent-optimized" structures, we recalculated the single point gas phase energies with the LACVP**++ basis set and the single point solvent energies with the LACVP** basis set.

Jaguar 6.5 is not capable of solving frequencies analytically under an implicit solvent, and so numerical algorithms are employed. Occasionally, we encountered small (less than 50 cm^{-1}) and/or extra imaginary frequencies relating to torsions of coordinated water molecules or other soft bending modes. Comparisons of these frequencies to those from gas phase calculations with analytic vibrational frequencies suggest that these discrepancies more likely attributed to Jaguar's frequency code rather than as an error with our geometries. Since we expect our optimized geometries to be accurate, E_{gas} and E_{solv} terms will be unaffected by these small frequencies. However, thermodynamic contributions, S_{vib} in particular, will be drastically affected by spurious small frequencies. In order to treat these cases consistently, we chose to replace all vibrational frequencies that were unexpectedly less than $50cm^{-1}$ with frequencies valued at $50cm^{-1}$ and recalculate ZPE, H_{vib}, and S_{vib} according to the standard procedure.[8]

(3) Validation calculations:

3.a) Validation of kinetic calculations: Ligand exchange barriers.

For the associative ligand exchange reaction barrier:

$$[Pd(II)(Cl)_4]^{2-} + H_2O \rightarrow [Pd(II)(Cl)_4(H_2O)]^{\ddagger -}$$

Leading to $[Pd(II)(Cl)_3(H_2O)]^- + Cl^-$, we use the following data:

H_2O
E_{gas} = -76.43312825144 Eh = -47962.5 kcal/mol
ZPE = 13.4 kcal/mol
$H_{vib} + 3*kT + pV$ = 2.4 kcal/mol
$-T*S_{H2O}$ = -13.9 kcal/mol
ΔG_{solv} = -2.1 kcal/mol
G = -47962.6 kcal/mol

$[Pd(II)(Cl)_4]^{2-}$
E_{gas} = -1967.726836 Eh = -1234767.3 kcal/mol
E_{solv} = -0.3009667 Eh = -188.9 kcal/mol
ZPE = 2.5 kcal/mol
$H_{vib} + 3*kT$ = 5.1 kcal/mol
$-T*S_{vib}$ = -6.4 kcal/mol
$kT*\ln(22.4)$ = 1.9 kcal/mol
G = -1234953.1 kcal/mol

$[Pd(II)(Cl)_4(H_2O)]^{\ddagger -}$
E_{gas} = -2044.156212 Eh = -1282727.4 kcal/mol
E_{solv} = -0.29941731 Eh = -187.9 kcal/mol
ZPE = 17.6 kcal/mol
$H_{vib} + 3*kT$ = 6.5 kcal/mol
$-T*S_{vib}$ = -9.4 kcal/mol

---

[5](a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623.
[6] Tannor, D.J.; Marten, B.; Murphy, R.; Friesner, R.A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W.A.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875.
[7] Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 270.
[8] See any physical chemistry textbook's chapter on statistical thermodynamics for equations of partition functions.

kT*ln(24.5) = 1.9 kcal/mol
G = -1282898.7 kcal/mol

Thus the barrier:

$$[Pd(II)(Cl)_4]^{2-} + H_2O \rightarrow [Pd(II)(Cl)_4(H_2O)]^{\ddagger-}$$

has a calculated $\Delta G^{\ddagger}$ = (-1282898.7 kcal/mol) – [(-1234953.1 kcal/mol) + (-47962.6 kcal/mol)] = 17.0 kcal/mol, which is in good agreement with the experimental barrier $\Delta G^{\ddagger}$ = 16 kcal/mol.[9] In a test set of 12 experimentally known barriers for associative Cl^-, H_2O ligand exchange reactions involving anionic and neutral Pd(II) or Pt(II),[10] this method was found to have an RMS error of 1.2 kcal/mol for barriers and 1.3 kcal/mol for relative ΔG values.

3.b) Deprotonation Calculations

3.b.1. <u>Using all-QM explicit H_3O^+</u>

To calculate deprotonation reactions entirely with QM, the most straightforward approach would be to include an explicit H_2O to the left and an explicit hydronium ion (H_3O^+) to the right in the balanced reaction. This allows all solvation energies to be calculated from QM. For example, the following reaction (which has a experimental $\Delta G^{\ddagger}$ = 9.6 kcal/mol)

$$[Pt(Cl)_3(H_2O)]^- + H_2O \rightarrow [Pt(Cl)_3(OH)]^{2-} + H_3O^+$$

Has the following computed values:

$[Pt(Cl)_3(H_2O)]^-$
E_{gas} = -1576.385745 Eh = -989197.0 kcal/mol
E_{solv} = -0.10808 Eh = -67.8 kcal/mol
ZPE = 18.1 kcal/mol
H_{vib} + 3*kT = 5.4 kcal/mol
$-T*S_{vib}$ = -7.0 kcal/mol
kT*ln(24.5) = 1.9 kcal/mol
G = -989246.5 kcal/mol

$[Pt(Cl)_3(OH)]^{2-}$
E_{gas} = -1575.727198 Eh = -988783.8 kcal/mol
E_{solv} = -0.31737 Eh = -199.2 kcal/mol
ZPE = 10.2 kcal/mol
H_{vib} + 3*kT = 5.1 kcal/mol
$-T*S_{vib}$ = -6.4 kcal/mol
kT*ln(24.5) = 1.9 kcal/mol
G = -988972.1 kcal/mol

H_2O
E_{gas} = -76.43312825144 Eh = -47962.5 kcal/mol
ZPE = 13.4 kcal/mol
H_{vib} + 3*kT + pV = 2.4 kcal/mol
$-T*S_{H2O}$ = -13.9 kcal/mol
ΔG_{solv} = -2.1 kcal/mol
G = -47962.6 kcal/mol

H_3O^+

[9] Gunther, R.G.; Martin, D.S.; *Inorg. Chim. Acta*, **1972**, *6*, 81
[10] Coe, J.S., MTP International review of science. Inorganic chemistry, **1974**, 45-62

E_{gas} = -76.70581677 Eh = -48133.6 kcal/mol
E_{solv} = -0.16034881 Eh = -100.6 kcal/mol
ZPE = 22.0 kcal/mol
H_{vib} + 3*kT = 1.8 kcal/mol
-T*S = -3.7 kcal/mol (S obtained from (45.9 cal/mol*K)^2 + (-33.6 cal/mol*K)[3a,c])
kT*ln(24.5) = 1.9 kcal/mol
G = -48212.2 kcal/mol

Thus, the relative free energy is:

ΔG = [(-988972.1 kcal/mol) + (-48212.2 kcal/mol)] – [(-989246.5 kcal/mol) + (-47962.6 kcal/mol)]
= 24.8 kcal/mol!

This result thus has an error of 15.6 kcal/mol, an obvious deficiency in this type of calculation, and likely the result of a poor description of the solvation energy of H_3O^+. Thermodynamic calculations on two other experimentally available deprotonations involving Pt complexes[1] [no thermodynamic data was found for Pd-(OH) complexes] found a mean-signed (average) error (-16.0 kcal/mol) and a RMS error (16.0 kcal/mol) that suggest this error is apparently a consistent under-estimation of the free energy of H_3O^+ by ~ 16 kcal/mol.

3.b.2. <u>Using experimental H_3O^+ solvation energies</u>

As we believe the description of H_3O^+ solvation is poor, we examined whether using the experimental solvation energy of H_3O^+ would improve the accuracy of the test calculations.

For the deprotonation reaction:

$$[Pt(Cl)_3(H_2O)]^- + H_2O \rightarrow [Pt(Cl)_3(OH)]^{2-} + H_3O^+$$

we calculate the relative energies:

$[Pt(Cl)_3(H_2O)]^-$ (see 3.b.1 above)
G = -989246.5 kcal/mol

$[Pt(Cl)_3(OH)]^{2-}$ (see 3.b.1 above)
G = -988972.1 kcal/mol

H_2O (see 3.b.1 above)
G = -47962.6 kcal/mol

H_3O^+
E_{gas} = -76.70581677 Eh = -48133.6 kcal/mol
ZPE = 21.6 kcal/mol
H_{vib} + 3*kT + pV = 2.4 kcal/mol
-T*S = -14.4 kcal/mol
G_{solv} = -110.2 kcal/mol
G = -48234.2 kcal/mol

In this approach, calculating the deprotonation of $[Pt(Cl)_3(H_2O)]^-$ leads to an free energy difference of

ΔG = [(-988972.1 kcal/mol) + (-48234.2 kcal/mol)] – [(-989246.5 kcal/mol) + (-47962.6 kcal/mol)]
= 2.8 kcal/mol

While this is a noticeable improvement over the QM solvation energy calculations (b.1), this is not satisfactory. For all three deprotonations involving Pt complexes[1] we calculated a mean signed error (-6.9

kcal/mol) and an RMS error 6.9 kcal/mol, suggesting that calculations in this mode are consistently in error by ~ 7 kcal/mol.

3.b.3. <u>Using experimental H^+ solvation energies</u>

An alternate approach would be to use the experimental energies for H^+ instead of the explicit hydronium.

For the deprotonation reaction:

$$[Pt(Cl)_3(H_2O)]^- \rightarrow [Pt(Cl)_3(OH)]^{2-} + H^+$$

we calculate the relative energies:

$[Pt(Cl)_3(H_2O)]^-$ (see 3.b.1 above)
G = -989246.5 kcal/mol

$[Pt(Cl)_3(OH)]^{2-}$ (see 3.b.1 above)
G = -988972.1 kcal/mol

H^+
$H_{gas} = 3*kT = 1.8$ kcal/mol
$-T*S_{gas} = -7.8$[2]
$G_{solv} = -254.0$ kcal/mol[3a]
G_{H+} = -270.3 kcal/mol

In this approach, calculating the deprotonation of $[Pt(Cl)_3(H_2O)]^-$ leads to an free energy difference of

$$\Delta G = [(-988972.1 \text{ kcal/mol}) + (-270.3 \text{ kcal/mol})] - (-989246.5 \text{ kcal/mol}) = 4.1 \text{ kcal/mol}$$

which is thus far the best agreement with the experimental value, 9.6 kcal/mol. For all three deprotonations involving Pt complexes[1] we calculated a mean signed error (-4.8 kcal/mol) and an RMS error 4.8 kcal/mol, suggesting that our calculations in this mode are consistently in error by ~ 5 kcal/mol.

3.b.4. *<u>Using an empirical correction for H^+ (or H_3O^+)</u>*
Since attempts at using calculated and experimental data were consistently in disagreement with basic experimental free energies, we have used an empirical correction to yield the best accuracy. Applying a correction of +4.8 kcal/mol to the experimental G of solvated H^+ leads to the value **-265.5 kcal/mol**, which, for the three reactions described above, yields a mean signed error of zero and an RMS error of 0.5 kcal/mol.

The above reaction is thus calculated to be:

$$\Delta G = [(-988972.1 \text{ kcal/mol}) + (-265.5 \text{ kcal/mol})] - (-989246.5 \text{ kcal/mol}) = 8.9 \text{ kcal/mol}$$

For the purpose of calculating this species p*Ka*, we obtain:

$$pKa = -\log[\exp(-\Delta G/kT)] = -\log[\exp(-(8.9)/.592)] = 6.5$$

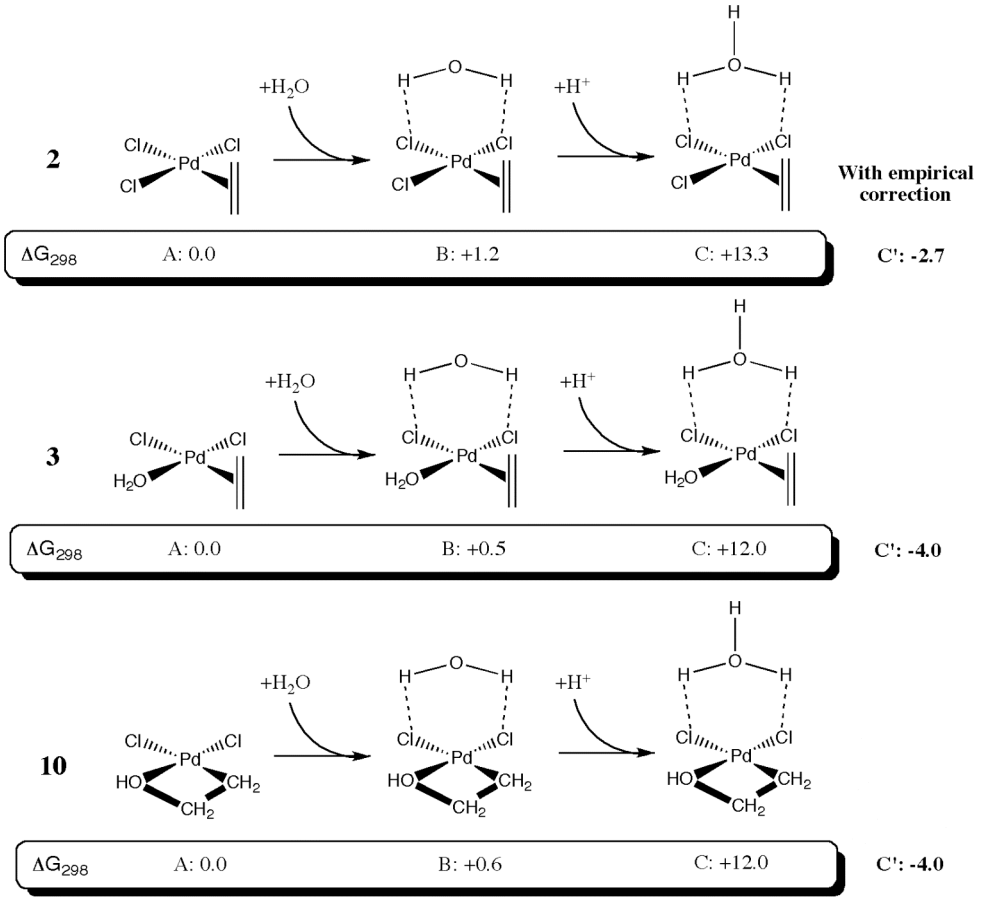
This empirical correction is identical to applying a correction of -16.0 kcal/mol to the free energy of the all-QM explicit H_3O^+ in **3.b.1**, or a correction of +6.9 kcal/mol to the free energy of H_3O^+ in **3.b.2**. *As a result, for generality, we carry out our relative energy calculations in the manner of **3.b.1**, but with a correction of -16 kcal/mol whenever there is an H_3O^+ present.*

3.c) Discussion of TS-INT and TS-ALE2

In our study, we encountered two transition states, **TS-INT** and **TS-ALE2**, which appear to be water-catalyzed in that running a simulation on analogs of these transition states without an explicit water are substantially higher in energy (~10 kcal/mol). However, even with the catalyzing water, the calculated energies of **TS-INT** and **TS-ALE2** are +33.8 kcal/mol and +34.0 kcal/mol, respectively. These barriers are much too high to be feasible in the Wacker process ($\Delta G^{\ddagger}$ = +22.4 kcal/mol), yet both transition states correspond to isomerizations that *must* occur in order for Wacker oxidized products to be formed. In both of these transition states an explicit H_3O^+ is formed, and based on the results of our validation calculations on explicit H_3O^+ (**section 3-b-1,2,3,4**), we believe an empirical correction must also be used in transition states where H_3O^+ is formed (i.e. T**S-INT** and **TS-ALE2)**.

The value of this correction is hard to determine due to a lack of available experimental data. In order to ascertain an approximate empirical correction for these transition states, we considered the complexes **2**, **3**, and **10** from the text of the article. In an ideal implicit solvation model, one should expect that the addition of explicit water to any complex should neither increase nor decrease the relative free energy of the water-bound complex. We find that the addition of a single water molecule does not greatly influence the free energy of any of these complexes, expectedly leading to small changes in energy (~ 1 kcal/mol, see figure S1). However, dramatic changes in energy (11.4 – 12.1 kcal/mol, see figure S1) are found when protonating the weakly bound explicit water to form an explicit hydronium. (Energies are calculated relative to the free energy of a proton infinitely separated from the water-bound complex (G_{H+} = -265.5 kcal/mol). This is an obvious error, since we would expect slightly binding interactions between these complexes an a nearby hydronium. This is particularly surprising in the case for intermediate **2**, which is an ion pair, and is thus expected to be qualitatively more stable than the infinitely separated species.

Since the apparent difference in energy seems to be consistent, we employed the empirical correction term of -16.0 kcal/mol to all intermediates and transition states involving an explicit H_3O^+ to minimize the errors in the calculation shown in **3-b-1**. To us, this correction seems qualitatively feasible since the energies C' in figure S1 are now all slightly binding (by ~ -3.5 kcal/mol) rather than very repulsive (by ~12.5 kcal/mol). This correction brings the energy of **TS-INT** and **TS-ALE2** to +18.0 kcal/mol and +17.8 kcal/mol, respectively, i.e. substantially lower in energy than the three competitive RDS transition states: **TS-EXT**, **TS-ALE1**, and **TS-ISO**, which all lie between 22.7 and 23.3 kcal/mol. Most importantly, this leads to kinetic equations that are consistent with the experimental observations, as both **TS-ALE2** and **TS-INT** *must* be lower in energy to yield the observed experimental rate laws. Although these corrected energies are not expected to have the same precision as the other barriers (i.e. the ones not involving an explicit H_3O^+), we are confident that our reported energies for **TS-INT** and **TS-ALE2** are at least qualitatively correct in that they are a few kcal/mol lower than 22.4 kcal/mol, the experimental activation energy of the Wacker Process, and thus not likely to play an effect under different ion concentrations.



All energies reported in kcal/mol

Figure S1: Calculated

3.d) Discussion of protonated alkyl-alcohol species 5-H and 9-H

Our mechanism contains two other protonated intermediates (**5-H** and **9-H**) that we considered might require empirical corrections. To determine the value of this correction we calculated the energy for protonation of methanol, and received an energy of -9.5 kcal/mol using -265.5 kcal/mol as the value for H^+. The experimental value is -3 kcal/mol (pKa = -2.2).[11] We thus concluded that in this study, an empirical correction term of +6.5 kcal/mol is warranted in protonated alkyl-alcohol species (**5-H** and **9-H**). Although this empirical correction has no impact on the deductions made in the investigation, it resolves the unlikely issue that the expectedly stable intermediate, **9-H**, would be isoenergetic with the entering and exiting transition states: **TS-EXT** and **TS-ALE2**.

Straightforward validation of this correction would be possible with the determination of the p*Ka*'s of the protonated forms: **5-H** and **9-H**. With our 6.5 kcal/mol correction, we calculate the p*Ka* of **5-H** to be -1.2 (rather than -6.3 with our otherwise best calculation), and the *pKa* of **9-H** to be -1.8 (rather than -7.0).

[11] See URL: http://daecr1.harvard.edu/pKa/ProtonatedOxygen.GIF

Geometries

Cl (-):

atom	x	y	z
Cl1	0.0000000000	0.0000000000	0.0000000000

H2O:

atom	x	y	z
O1	-0.0015631424	0.0000000000	-0.0011819611
H2	0.0184539530	0.0000000000	0.9662883823
H3	0.9351730873	0.0000000000	-0.2440265092

H3O (+):

atom	x	y	z
H1	-0.1239153334	0.5097395021	0.0214904439
O2	-0.4024202537	1.4492031706	-0.0012527579
H3	-1.3574457941	1.4997715592	0.2129760672
H4	0.0993102936	1.9440335993	0.6798496661

C2H4:

atom	x	y	z
C1	-0.0000001304	0.0000000077	-0.6653584680
C2	-0.0000000777	-0.0000000361	0.6653584539
H3	0.0000005065	0.9235262207	1.2383150580
H4	0.0000007180	-0.9235260389	1.2383156310
H5	0.0000007321	0.9235265243	-1.2383151263
H6	0.0000005205	-0.9235263688	-1.2383153948

PtCl2(OH)2 (2-)

atom	x	y	z
Pt1	0.0130515438	-0.0217359820	-0.0043275939
Cl2	-0.2134730164	-0.1073679863	2.4186483817
Cl3	2.4362286170	0.2034227198	-0.0636902502
O4	0.0447147781	0.0343640610	-2.0258062580
H5	0.9799403651	0.1594368441	-2.2464036353
O6	-1.9979890719	-0.1989390788	-0.1116943152
H7	-2.2821894288	-0.2835927682	0.8107457522

PtCl2(OH)(H2O) (-)

atom	x	y	z
Pt1	0.0174127231	-0.0279515427	-0.0088219901
Cl2	-0.0020833743	0.1220419871	2.4130752935
Cl3	2.3537118688	0.0670620794	-0.1659909016
O4	-0.1019240072	-0.1292947126	-2.0079002571
H5	0.8138825083	-0.1759441331	-2.3233426523
O7	-2.1175370224	-0.1036707875	0.0042011197
H8	-2.4522308754	0.0265924370	-0.9012074942
H9	-2.4171733110	-0.9933013300	0.2614502403

PtCl2(H2O)2

atom	x	y	z
Pt1	0.0204794901	-0.0152210731	-0.0133693368
Cl2	-0.1666988736	-0.4114246072	2.2796200071
Cl3	2.3494655792	0.1215191388	0.0579984785
O4	0.1131130631	0.3430421830	-2.1065148619
H5	0.7136661528	1.0875003411	-2.2964661970
H6	0.5021953648	-0.4268237887	-2.5611847320

O7	-2.0973984699	-0.1214865185	-0.1529627331
H8	-2.4164725873	-0.9603194966	0.2275458257
H9	-2.5043071915	0.5818971878	0.3856320127

PtCl3(OH) (2-)

atom	x	y	z
Pt1	-0.0024890338	-0.0019876432	-0.0002771688
Cl3	2.3930372781	-0.0036350656	0.0353867169
Cl4	0.0047326149	-0.0072834047	-2.4364324218
Cl5	-2.3857418430	-0.0011966840	0.1145230533
O5	-0.0031351950	-0.0006346110	2.0147335043
H6	-0.9452780955	-0.0108418685	2.2434730103

PtCl3(H2O) (-)

atom	x	y	z
Pt1	-0.0129409821	0.0043353295	-0.0189020936
Cl3	2.3650292738	0.0661734605	0.0256206666
Cl4	-0.0283770354	0.0282393490	-2.3602606007
Cl5	-2.3889144910	-0.0252949935	0.1039338337
O5	-0.0127852818	0.0075656786	2.1091660875
H6	-0.9320653338	0.1161831937	2.4180321656
H7	0.2682778672	-0.8657474364	2.4366966331

CuCl2(H2O)2:

atom	x	y	z
Cu1	0.3524360655	1.4324780511	-0.2194822690
Cl2	1.7632988535	-0.2289546391	0.5398337339
Cl3	-1.0581125509	3.0943465838	-0.9786742814
O4	1.5321001789	2.8153004655	0.6146104424
H5	2.4672607747	2.5470195944	0.6429221934
H6	1.5039794014	3.6703522141	0.1503973159
O7	-0.8269765617	0.0494289773	-1.0542039043
H8	-0.8025309526	-0.8055189191	-0.5897889407
H9	-1.7617703737	0.3177697073	-1.0881415585

1: PdCl4 (2-)

atom	x	y	z
Pd1	-0.0000660000	0.0000010000	0.0022880000
Cl2	2.3901210000	0.0001120000	0.0165700000
Cl3	-0.0000350000	2.3915170000	-0.0200710000
Cl4	-2.3899040000	0.0001770000	0.0166270000
Cl5	0.0000200000	-2.3918080000	-0.0200460000

Cu-1:

atom	x	y	z
Pd1	-0.0532851463	0.0011718782	0.0575053415
Cl2	0.0262535273	-0.0572689817	2.4097763196
Cl3	2.3445225892	0.0687880928	-0.0971292562
Cl4	0.0125219551	0.0672672674	-2.3455474552
Cl5	-2.4062336812	-0.0588308884	0.0626876601
Cu6	2.4097812656	0.1121770127	-2.5008785257
Cl7	2.2761652322	0.0917836195	-4.7911291166
Cl8	4.7013237872	0.2015373526	-2.4419838942

2: PdCl3(C2H4) (-)

atom	x	y	z
Pd1	-0.6165650000	5.2331810000	2.5702650000

Cl2	1.4703030000	6.2284040000	2.0238250000
Cl3	-0.3322830000	3.6085670000	0.8223940000
Cl4	-2.7093400000	4.2747110000	3.1594970000
C5	-1.1752300000	7.0820130000	3.6847980000
C6	-0.5404500000	6.2277680000	4.5659740000
H7	-2.2579390000	7.1120420000	3.6195770000
H8	-0.6266450000	7.8703460000	3.1798760000
H9	-1.1102880000	5.5672850000	5.2113980000
H10	0.5205270000	6.3255480000	4.7716510000

2_H2O:

atom	x	y	z
Pd1	-0.0753873966	0.0496087169	-0.0311026970
Cl2	0.4504971876	-0.2024868412	2.2666877897
Cl3	2.1648613936	0.8236886527	-0.4635432084
Cl4	-0.6613741353	0.3007324191	-2.3264894901
C5	-2.2492759919	0.0400807734	0.4948175496
C6	-1.8568800513	-1.2654596330	0.2686381187
H7	-2.7144961060	0.6273840633	-0.2902973653
H8	-2.2760853888	0.4485976185	1.5000301640
H9	-2.0066522331	-1.7335849966	-0.6990572313
H10	-1.5681187779	-1.9110096786	1.0919138329
H11	2.1751014566	2.2241319936	-2.4864387332
O12	1.6844799492	2.4833915004	-3.2817847643
H13	0.8893202900	1.9328123189	-3.1997784182

2_H3O:

atom	x	y	z
Pd1	1.8464959489	1.2098382281	0.4299651542
C2	0.2103802638	0.3628151174	-0.8302429931
C3	-0.0418085983	0.0116083943	0.4848737611
Cl4	3.1462069287	-0.7728905830	0.0249341542
Cl5	0.5512778477	3.1460107794	0.7784721692
Cl6	3.8445931089	2.4258815331	1.1556993246
O7	5.7332048177	0.7290879325	-0.3603179151
H8	0.7183153576	-0.3218621647	-1.5021892330
H9	-0.2608274484	1.2344549241	-1.2737735324
H10	0.2617210524	-0.9545696502	0.8768353210
H11	-0.7154594481	0.6026095318	1.0976312873
H12	5.2910119029	1.4992013289	0.1288548651
H13	4.9930581903	0.0631964401	-0.4891909902
H14	6.0474385708	1.0372043538	-1.2354282432

Cu-2:

atom	x	y	z
Pd1	-0.0749781277	0.0570612922	0.0154861753
Cl2	0.0158706841	0.0192724845	2.3592446878
Cl3	2.3470890838	0.2413401239	-0.1718555597
Cl4	-0.0349191096	0.1174221526	-2.3763784912
C5	-2.2332659691	0.5962912434	0.0928667386
C6	-2.1349887310	-0.7848632296	0.0646085045
H7	-2.3982352249	1.1666093789	-0.8169062781
H8	-2.3392797383	1.1283795253	1.0330812909
H9	-2.2206027497	-1.3353413735	-0.8680614476
H10	-2.1622609898	-1.3646539972	0.9819223905
Cu11	2.3857010447	0.3292406569	-2.5753721444
Cl12	4.6719418669	0.4746340092	-2.5677185263

Cl13	2.1920921849	0.4297501075	-4.8514976937

TS-ALE1 (-)

atom	x	y	z
Pd1	0.0021692122	0.0010295522	-0.0012462558
Cl2	-0.0002224452	-0.0025011646	2.8411763612
O3	2.2779967884	-0.0000980822	0.8803809776
Cl4	0.4026797562	-2.3551196088	-0.0878642113
Cl5	-1.4526631637	-0.1577044491	-1.8556198764
C6	0.2380453902	2.1814413645	-0.4294662565
C7	-0.8724508757	2.0512756450	0.3798363953
H8	0.1398002819	2.2474590128	-1.5085311043
H9	1.2112661524	2.4160100790	-0.0085689334
H10	-1.8697498351	1.9917008149	-0.0448988160
H11	-0.7992169465	2.1677699871	1.4548326167
H12	1.9363028711	-0.0277174707	1.7994156423
H13	2.5048003471	-0.9264051024	0.6901539305

Cu-TS-ALE1 (-)

atom	x	y	z
Pd1	0.0326581783	0.0064869938	-0.0138612888
Cl2	-0.0186363341	-0.0474106759	2.7781578153
O3	2.2553038373	0.0300165459	0.8279327706
Cl4	0.1828286053	-2.3990692441	-0.0665084389
Cl5	-1.5463057784	-0.2711315886	-1.7832846678
C6	0.2666997188	2.1567253228	-0.5319423473
C7	-0.7880356594	2.0750553307	0.3599326063
H8	0.0962784925	2.1915274740	-1.6040911989
H9	1.2683489221	2.3913943015	-0.1840193869
H10	-1.8168182343	2.0146007524	0.0143718075
H11	-0.6385096947	2.2310322432	1.4222858529
H12	1.9681656682	-0.0647273733	1.7609213420
H13	2.6656968026	-0.8231484228	0.6079376629
Cu14	-1.3240406385	-2.6964254286	-1.9146356640
Cl15	-2.9344565411	-2.7496541924	-3.5287985741
Cl16	-0.8487967504	-4.9292073252	-2.0009679877

3: PdCl2(C2H4)(H2O)

atom	x	y	z
Pd1	-0.0266608460	-0.0309329670	0.0124664773
O2	-0.3474583555	-0.0760516226	2.1106686573
C3	1.8595581943	-1.2282017606	0.2808201647
C4	2.1931073401	0.1086644888	0.3603081077
Cl5	0.3444789020	0.0115973059	-2.2836561295
H6	-1.0858110274	-0.6799930191	2.3106297008
H7	2.5729552492	0.6425688976	-0.5055615370
H8	2.2576329384	0.6147110266	1.3196755255
H9	1.6544263675	-1.8088831933	1.1759194584
H10	1.9713233474	-1.7776757549	-0.6490876236
Cl11	-2.3222365476	0.5635195145	-0.2617154747
H12	-0.6559938731	0.7994137037	2.4076625463

3_H2O:

atom	x	y	z
Pd1	-0.0241741715	-0.1183739031	0.0240369387
O2	0.0515697587	-0.4859954701	2.0905505018
C3	2.1099395424	0.5803052255	0.0266845066

C4	1.3128625519	1.6532991480	0.3718535674
Cl5	-0.1385994012	0.3599422358	-2.2597170841
H6	-0.1008041765	-1.4359895394	2.2411986501
H7	1.0001186163	2.3834045776	-0.3690516126
H8	1.1350867012	1.9023409791	1.4146522322
H9	2.5731871249	-0.0414836718	0.7874630696
H10	2.4434395917	0.4414441935	-0.9970320103
Cl11	-2.0233013950	-1.4347098256	-0.0427181874
H12	-0.7718182390	-0.0099692560	2.4336641860
O13	-2.1133310656	0.8612302990	2.7140879564
H14	-2.0288102151	1.7980054725	2.4746629343
H15	-2.7987716644	0.5266774621	2.1132818512

3_H3O:

atom	x	y	z
Pd1	0.0209534041	-0.0064367609	0.0375991743
O2	0.2357302215	-0.6380537074	2.0345959536
C3	2.1552390650	-0.6192752876	-0.3185737567
C4	2.1695321195	0.6871247921	0.1330429711
Cl5	-0.1124370366	0.7762214250	-2.1667783152
H6	-0.3161763785	-1.4162652950	2.2323441516
H7	2.2337466434	1.5202755585	-0.5610576314
H8	2.3085682761	0.9110423262	1.1875405488
H9	2.2804669514	-1.4491100996	0.3717720248
H10	2.2089034605	-0.8440485927	-1.3798148608
Cl11	-2.3944626509	-0.0459222385	0.2661095832
H12	-0.0564200895	0.0515924635	2.6585024197
O13	-3.2067486229	0.8662624164	-2.4723439908
H14	-3.1810897971	0.4226047428	-1.5673425848
H15	-2.2551160872	0.9451089329	-2.7477534326
H16	-3.6710266593	0.2850860949	-3.1125837573

Cu-3:

atom	x	y	z
Pd1	0.0355069536	0.0425536674	0.0783237090
O2	0.0810602482	0.0498915397	2.1769859459
C3	2.2762783367	-0.0679774284	0.0397330949
C4	1.9162886978	1.2676060250	0.0393084605
Cl5	-0.0712660240	0.0216977968	-2.2568155151
H6	-0.1931144446	-0.8116493028	2.5412668893
H7	1.8613721791	1.8337989675	-0.8867613089
H8	1.8597648242	1.8322729851	0.9659988972
H9	2.5103157017	-0.5846733430	0.9665680373
H10	2.5131060925	-0.5858151257	-0.8859682495
Cl11	-2.2974796879	-0.5949984191	0.0125859541
H12	-0.5494832929	0.6983674388	2.5408888967
Cu13	-2.4437740238	-0.6109566827	-2.3982360142
Cl14	-2.2980519807	-0.5793341859	-4.6688598297
Cl15	-4.6567145215	-1.1555843742	-2.3230794152

4: PdCl2(C2H4)(OH) (-)

atom	x	y	z
Pd1	-0.0068389318	0.0103473948	0.0003301203
O2	-0.2109150083	0.1136649729	1.9652609135
C3	1.7266238022	-1.3439085041	0.3263636581
C4	2.1948566271	-0.0447150965	0.3086574223
Cl5	0.3035032354	-0.1436926109	-2.3923859755

H6	2.6093791390	0.3880751692	-0.5963480057
H7	2.3404434487	0.5090542735	1.2303911483
H8	1.4942999746	-1.8407729068	1.2626779084
H9	1.7614867383	-1.9628546413	-0.5645250397
Cl10	-2.2697720653	0.8405422173	-0.1822111340
H11	-1.1183515718	0.4429906046	2.0699441053

Cu-4:

atom	x	y	z
Pd1	0.0301275226	0.0254278080	-0.0249436856
O2	-0.0254933197	-0.0218320148	1.9386570028
C3	2.2516276120	-0.0101488296	0.1346670375
C4	1.8419130243	1.3100986768	0.1552632883
Cl5	0.0070874377	0.0547216243	-2.4537840641
H6	1.8486146603	1.9151355030	-0.7472230568
H7	1.6875308007	1.8319893853	1.0942763788
H8	2.4289274503	-0.5537412092	1.0571832997
H9	2.5920039212	-0.4788287555	-0.7846955312
Cl10	-2.2900062358	-0.6874009800	-0.2192208201
H11	-0.9330196580	-0.2947316446	2.1520030018
Cu12	-2.2695786864	-0.7471310130	-2.6388622351
Cl13	-4.4264456678	-1.5222279037	-2.6410525052
Cl14	-2.0972221633	-0.7293521841	-4.9233266455

TS-EXT (-)

atom	x	y	z
Pd1	0.0014408856	0.0019648834	-0.0132603400
C2	-0.0673087618	-0.0063782770	2.6661403486
O3	0.4619841117	-0.0101849020	4.3883938397
C4	1.0699755328	0.0049416790	1.7798743203
H5	1.0181662379	0.7772986146	4.5428904630
Cl6	0.0126044115	-2.3934865244	0.0855154971
H7	1.6690325321	-0.9034453135	1.7766557848
H8	1.6566323326	0.9215533126	1.7829728439
Cl9	-1.0829374711	-0.0043905958	-2.2613096588
Cl10	-0.0262116058	2.3974718486	0.0937726415
H11	-0.6595917509	0.8996155127	2.7475054480
H12	-0.6466135469	-0.9214493864	2.7400375466
H13	1.0528049047	-0.7748274880	4.5269303805

Cu-TS-EXT (-)

atom	x	y	z
Pd1	-0.0275465090	0.0119282955	0.0312413165
C2	-0.0342277438	0.0179008157	2.7497762492
O3	0.5911613452	-0.0054499860	4.4107278616
C4	1.0627042964	0.0105324864	1.7995356727
H5	1.1472614481	0.7873408026	4.5445409558
Cl6	-0.2494990724	-2.3886780602	0.0642094733
H7	1.6550034676	-0.9049248379	1.7779639045
H8	1.6660199375	0.9166035653	1.7911006830
Cl9	-1.1907694599	-0.1894671326	-2.1884722231
Cl10	0.0955083114	2.3744119581	-0.0093791692
H11	-0.6044633439	0.9357920071	2.8591517664
H12	-0.6343749660	-0.8819643342	2.8489784586
H13	1.1960941254	-0.7675209006	4.5045276792
Cu14	-1.6610254943	-2.5064959465	-1.8928063668
Cl15	-1.5711407767	-4.7983011411	-1.8666380396

Cl16	-3.3985175256	-2.4151648431	-3.3926431271

9: PdCl3(CH2CH2OH) (2-)

atom	x	y	z
Pd1	-0.0032066787	-0.0496032641	-0.0419354759
C2	0.1955810307	0.0632945706	2.8983287068
O3	1.3606148282	0.8922675760	2.8520811934
C4	-0.7983074485	0.3598572098	1.7960288487
Cl5	0.9531905530	2.1896171908	-0.0610745472
H6	-1.0872132360	1.4150868767	1.7873519806
H7	-1.6836969156	-0.2716389028	1.8948604497
Cl8	0.9892918958	-0.5749197446	-2.3836403449
Cl9	-0.8870181945	-2.2870035013	0.1903212670
H10	-0.2738994920	0.2332077013	3.8802367615
H11	0.4779569847	-0.9986916617	2.8651194674
H12	1.4694457451	1.1738674419	1.9260740240

Cu-9:

atom	x	y	z
Pd1	0.2307474577	0.5097502704	-0.1536035306
C2	-0.5127450950	-0.2253992966	2.5821398908
O3	0.5387091644	-1.1866912676	2.6833827484
C4	-0.1284624126	1.0054010044	1.7907161963
Cl5	2.5157729189	0.0218970125	0.3811938884
H6	0.7823969525	1.4734555493	2.1731251605
H7	-0.9463618032	1.7313391398	1.7646229939
Cl8	0.3643248753	-0.1323006055	-2.7002866857
Cl9	-2.1012177776	0.8471640635	-0.7423065620
H10	-0.7699056158	0.0663304811	3.6116369446
H11	-1.4154704369	-0.6796637951	2.1483637274
H12	1.0557314823	-1.1305078741	1.8612735886
Cu13	-1.9868355005	-0.3599651399	-2.8427357839
Cl14	-4.2941063920	-0.4622813252	-2.8634035283
Cl15	-1.7978816657	-1.5660045849	-4.8130556142

9H: PdCl3(CH2CH2OH2) (-)

atom	x	y	z
Pd1	0.0067542800	-0.1141766757	-0.0240372975
C2	0.5014567247	-0.0261435045	2.9757624550
O3	1.4445774321	1.1403780695	3.0477428107
C4	-0.5635622635	0.1598048569	1.9241397527
H5	1.0279775126	1.9146032275	3.4779951946
Cl6	1.8895156466	1.4374068061	0.2487078063
H7	-1.0154706369	1.1572958263	1.9886773010
H8	-1.3405890758	-0.5849334967	2.1121597145
Cl9	0.6756297610	-0.4468436781	-2.4746497472
Cl10	-1.8599014533	-1.6160341237	-0.2444820675
H11	0.0954707599	-0.0951750739	3.9884942918
H12	1.1567275442	-0.8795178658	2.7969180751
H13	1.7184039666	1.4000602212	2.0824555290

Cu-9-H:

atom	x	y	z
Pd1	-0.1723404740	-0.1911072232	-0.3976713835
O2	0.1055836324	0.2995370429	2.9935423587
Cl3	2.1628100500	0.3704978093	-0.2885024741
Cl4	-0.6811501678	1.5490632967	-2.3561609501

C5	0.0198788077	-1.3986006553	1.2324472948
C6	-0.6274645872	-0.8512100872	2.4818056410
H7	-0.4841418128	-2.3225636024	0.9324926127
H8	-1.6717858227	-0.5746305439	2.3147804352
H9	-0.5965034376	-1.6197671788	3.2662605538
H10	0.3998016220	1.4054069466	2.2313032597
Cl11	-2.5902853412	-0.5152464796	-0.4652387217
O12	0.7686402900	2.2624169905	1.6715879838
H13	1.3922615550	1.9049307834	0.9835301811
H14	0.0266386395	2.7379027608	1.2009469066
H15	-0.2748991048	0.5597007253	3.8494639473
H16	1.0879069513	-1.5780867817	1.3692002503
Cu17	-2.4880574430	1.8743295798	-0.9083840340
Cl18	-4.6971842335	2.3415681188	-0.6760318141
Cl19	-1.5803493912	3.6639150562	0.3072715008

10: PdCl2(CH2CH2OH) (-)

atom	x	y	z
Pd1	0.0645328067	0.0306009747	-0.0364531969
O2	-0.1875351281	-0.1624449217	2.1310921476
C3	1.2845704618	-0.0130312488	2.2987367556
C4	1.8510048048	-0.1081866369	0.8918473923
Cl5	0.9640234828	-0.0561444019	-2.2367166012
H6	-0.4266123755	-1.0947364981	2.2683735207
H7	2.2973980470	-1.0733608811	0.6405994739
H8	2.4941916510	0.7219888072	0.5966765258
H9	1.4170227540	0.9751502749	2.7436764324
H10	1.6373154290	-0.7725313729	3.0005205052
Cl11	-2.3909160829	0.2301007426	-0.7414052861

10_H2O:

atom	x	y	z
Pd1	-0.0147241713	-0.1588252533	-0.0157745421
O2	-0.2875963600	-0.2084977700	2.1138169093
C3	1.0862737004	0.2862887267	2.3092603595
C4	1.3811546889	0.9295490342	0.9596903853
Cl5	0.7425218320	0.3598838397	-2.2095016752
H6	-0.4695317330	-1.1444180593	2.4110053145
H7	2.3794539015	0.7486838140	0.5603243032
H8	1.1042377822	1.9861108650	0.8972376151
H9	1.0927336456	0.9698989040	3.1655875280
H10	1.7475705174	-0.5579415500	2.5194943507
Cl11	-1.8481591963	-1.9081645639	-0.6094128872
O12	-1.3396239293	-2.6006964796	2.4379381057
H13	-2.1529430608	-2.4429765554	2.9428366505
H14	-1.6307047203	-2.5786955094	1.5008328940

10_H3O:

atom	x	y	z
Pd1	1.7767878998	0.8199455619	0.0900921196
C2	0.1314434462	-0.3532113455	0.0056934644
C3	-0.1669297070	-0.3470774060	1.4902808747
O4	1.1588755750	0.0370450420	2.1295571585
Cl5	3.8004946079	2.2081378188	0.7299693696
Cl6	1.7801010028	1.1407057062	-2.2480756807
H7	1.0297333754	0.7499026555	2.7863008992
H8	-0.6481249479	0.1039135900	-0.6072186561

H9	0.4221544609	-1.3297090815	-0.3915065681
H10	-0.4653152279	-1.2994620583	1.9351314761
H11	-0.8672082738	0.4342114615	1.7793640332
H12	1.9044314657	-0.9901820960	2.7164727610
O13	2.5143304400	-1.7648700346	3.1376385913
H14	2.0564862907	-2.2482506988	3.8508389073
H15	2.8068601366	-2.4326243952	2.4868780084

Cu-10:

atom	x	y	z
Pd1	0.0152475522	-0.1993419374	-0.0099719313
O2	0.0847325145	-0.5073092598	2.1323363152
C3	1.4307006648	0.1282707541	2.1821782654
C4	1.8403253363	0.2414926019	0.7237646385
Cl5	0.4276182802	0.3445554193	-2.3038581804
H6	0.1756339713	-1.4617384641	2.2969443328
H7	2.5252748126	-0.5351224602	0.3755809056
H8	2.1410379148	1.2388498646	0.3982553471
H9	1.2700346514	1.1005224169	2.6516951280
H10	2.0874384717	-0.4771766249	2.8117455249
Cl11	-2.3713603894	-0.7219107832	-0.9048591313
Cu15	-1.7667434056	-0.2477663203	-3.1571160230
Cl16	-3.8128011854	-0.9939913243	-3.9253393054
Cl17	-1.0777997057	0.4089461735	-5.2574562442

6: PdCl2(CH2CH2OH) (-)

atom	x	y	z
Pd1	0.0424197897	-0.0399061886	-0.0187283677
Cl2	-0.2274274225	0.0030039754	2.4921600313
Cl3	2.4148630075	0.1174604886	-0.2698925618
H4	-1.8688982965	-0.1908507114	-0.5152716859
O5	-2.3826928143	1.2478190620	-1.8640178513
C6	-0.3205372935	-0.0942069708	-2.0008745735
C7	-1.7680991711	-0.0072534692	-1.6564238338
H8	-2.2830028059	1.4767169676	-2.8012380506
H9	0.0267440319	-1.0485319319	-2.4008143933
H10	0.1009363216	0.7752456080	-2.5085891505
H11	-2.3611547097	-0.8470316735	-2.0476932891

Cu-6:

atom	x	y	z
Pd1	-0.0011985177	0.0410265674	-0.0424122838
Cl2	0.0167673164	0.0749418725	2.5015081716
Cl3	2.4167726568	0.0925704425	0.2233261594
H4	-1.7082942468	-0.0509857007	-0.5454289441
O5	-2.1974811179	1.4024696348	-2.0200748589
C6	-0.2020945462	0.0565935375	-2.0632126550
C7	-1.6360058528	0.1589964210	-1.7610492100
H8	-3.1357262284	1.3856053012	-1.7737021024
H9	0.1508892477	-0.9028742906	-2.4411151647
H10	0.2791217899	0.9325085996	-2.5007968578
H11	-2.2435057488	-0.6916246589	-2.0933373267
Cu15	2.4035986624	0.0156419522	2.6417199770
Cl16	2.2990193667	-0.0562491552	4.9509239849
Cl17	4.7064902793	-0.0356362422	2.6316203091

TS-ISO

atom	x	y	z
Pd1	0.0000000000	0.0000000000	0.0000000000
H2	0.0000000000	0.0000000000	2.9308070000
O3	1.8929140000	0.0000000000	2.1918670000
Cl4	-0.5257600000	-1.8704140000	-1.6425770000
Cl5	-0.9829820000	1.5924300000	-1.4748430000
C6	0.1519350000	1.4700780000	1.3571690000
C7	0.7141750000	0.7386050000	2.5495910000
H8	2.5535060000	0.6370160000	1.8775170000
H9	-0.8361640000	1.9029850000	1.5326870000
H10	0.8410000000	2.2110530000	0.9388510000
H11	0.9154050000	1.4435350000	3.3728810000

Cu-TS-ISO

atom	x	y	z
Pd1	-0.0838323947	-0.0244730600	-0.1400626644
Cl2	-0.0238618050	0.0182541847	2.3277914088
C3	1.9205154124	0.0830418695	-0.0742182304
C4	2.4182281323	0.0867548919	-1.4924921927
Cl5	-2.7155289105	-0.2561970275	0.2587798259
H6	1.9576921207	-0.7226390241	-2.0751622023
O7	2.1253302867	1.3031203429	-2.1781877204
H8	2.5602449200	2.0223978247	-1.6941291313
H9	2.2486110928	-0.7987404575	0.4874125972
H10	2.1589366979	1.0055659469	0.4683444267
H11	3.5032982807	-0.1215864861	-1.4908046307
Cu12	-2.3977246241	-0.0799684442	2.6059247891
Cl13	-2.4701554801	1.3490843974	4.4011864953
Cl14	-4.0458141150	-1.5223310178	3.2865661876

TS-INT:

atom	x	y	z
Pd1	-0.0091132702	-0.0178199709	-0.0354898588
O2	0.0501490120	-0.0318088717	2.1215748851
C3	1.9151394266	0.0083054796	1.8336984350
C4	2.0307416828	-0.0193995154	0.3973812908
Cl5	0.3616342331	0.1044241093	-2.3455328354
H6	-0.2493204092	-0.8432869337	2.5720014178
H7	2.4264040931	-0.9401017550	-0.0274422292
H8	2.4039599772	0.8978014840	-0.0566793403
H9	2.0645309969	0.9402357899	2.3715408407
H10	2.1044423065	-0.8939709573	2.4084482889
Cl11	-2.4774787662	0.2272253084	-0.1559555544
H12	-0.5324804397	0.8301095578	2.3791045774
O13	-1.4332594986	1.9265106278	2.3730496727
H14	-1.0120267410	2.7737388531	2.1518267484
H15	-2.0289286274	1.7260726297	1.6203597759

Cu-TS-INT

atom	x	y	z
Pd1	-0.0611579095	-0.2692364318	0.0169877099
O2	-0.0254990405	0.2861591658	2.0647385160
C3	1.8946870464	0.2943775337	1.7593983924
C4	1.9832794743	-0.0529892915	0.3686639751
Cl5	0.1482099554	-0.6014865319	-2.3207858935
H6	-0.2952434563	-0.3913262882	2.7124733079
H7	2.3932088807	-1.0393757442	0.1519083693

H8	2.2966936837	0.7479740419	-0.3001072953
H9	2.0127483980	1.3266564716	2.0765149461
H10	2.0808603039	-0.4580768976	2.5204965405
Cl11	-2.5228977607	-0.3728833461	-0.3852562322
H12	-0.5666430318	1.1966265240	2.1844262103
O13	-1.3579595611	2.3729333191	2.2515724388
H14	-1.1670119925	3.0355908413	1.5672098729
H15	-2.3104326645	2.1933814915	2.1794302436
Cu16	-2.0910090009	0.3566244888	-2.6239197405
Cl17	-4.2608012456	0.2272028694	-3.3203090413
Cl18	-1.4203190225	2.0082285219	-4.0475810146

Hydroxypalladation TS:

atom	x	y	z
Pd1	-0.0140093580	0.0176391773	-0.0017319756
O2	-0.0189741901	-0.0175187362	2.0346461716
C3	2.0967728775	-0.0116415170	1.4770885699
C4	2.1624047708	-0.1717744878	0.0991198685
H5	-0.1557703361	-0.9612021452	2.2217305720
H6	2.3422730605	-1.1606655020	-0.3146429164
H7	2.4345416378	0.6774837291	-0.5219002728
H8	2.1842007893	0.9745815542	1.9212342617
H9	2.1866371323	-0.8541115592	2.1523363142
Cl10	-2.4559053139	0.2609711034	-0.0729247854
Cl11	0.1546648931	0.0985201721	-2.3970724774

TS-INT (only 1 water)

atom	x	y	z
Pd1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.0432300070
C3	1.6383812571	0.0000000000	2.0529298760
C4	1.9512668630	-0.0428888267	0.6024348135
Cl5	0.5597421823	-0.0027998153	-2.2793097598
H6	-0.3797603328	-0.7971998956	2.4819920516
H7	2.4019592338	-0.9756028792	0.2633331089
H8	2.4562779289	0.8459018269	0.2247186685
H9	1.8429038742	0.9265836627	2.5853115428
H10	1.8453346624	-0.8864626201	2.6489307465
Cl11	-2.4750087999	0.0415842925	-0.3545660505
H12	-0.3846129406	0.7856351509	2.4977588026

TS-ALE2:

atom	x	y	z
Pd1	-0.0018811115	-0.0010569753	0.0025763045
O2	0.0027036587	-0.0000348539	2.5803523467
Cl3	3.0892184722	0.0040404167	0.6913799214
Cl4	0.3368933575	2.5619486137	-0.5224244300
C5	-0.2717189141	-1.7624480203	0.9341263203
C6	0.2623674009	-1.4238747875	2.3124637240
H7	-1.3440919920	-1.9749974211	0.9139421373
H8	0.2928240167	-2.5476394463	0.4250777187
H9	-0.1820953348	-2.0262052431	3.1133299449
H10	1.3468505128	-1.5184325822	2.3534166156
H11	0.9718665447	1.3818895232	2.4740576380
Cl12	-1.2069736872	-0.8141516568	-1.9012956620
O13	1.6228369674	2.0438107495	2.0854280102
H14	2.3207297336	1.4248708483	1.6243820044

H15	1.1390553549	2.4755895577	1.3031099990
H16	-0.9429978473	0.1344955909	2.7571873463

Cu-TS-ALE2

atom	x	y	z
Pd1	-0.1381030625	0.3215454477	0.1522038907
O2	0.1839568646	-0.1584613065	2.8970422698
Cl3	2.5215968089	0.4646089092	0.3584750028
Cl4	-0.2666601181	2.6559978284	-0.9770091858
C5	-0.0964479581	-1.5498157386	0.9071655730
C6	0.5038391239	-1.4524888634	2.3011301766
H7	-1.1446684346	-1.8672734860	0.9061405541
H8	0.5022219073	-2.1790401530	0.2383779868
H9	0.1585132695	-2.2537086193	2.9678902711
H10	1.5941989926	-1.4886190761	2.2605356352
H11	1.1958432514	1.0911429069	3.0777866098
Cl12	-1.7635224292	-0.2880631713	-1.6460211094
O13	1.8386193806	1.8300359424	2.7895998498
H14	2.2924252055	1.4336894385	1.9453463189
H15	1.3319379709	2.6284724183	2.5411547121
H16	-0.7120812119	-0.1629596028	3.2732941282
Cu17	-1.2583024137	1.6906859515	-2.9094497765
Cl18	-2.9922119488	1.3399388538	-4.3712142823
Cl19	0.1020562509	2.8155010003	-4.4074189994

	B3LYP//LACVP**++ **SCFE (Eh)**	B3LYP//LACVP** **Esolv (Eh)**	B3LYP//LACVP** **ZPE (kcal/mol)**	B3LYP//LACVP** **Htot (kcal/mol)**	B3LYP//LACVP** **Stot/vib (cal/mol*K)**	**Gcorr (kcal/mol)**	**H (kcal/mol)**	**G (kcal/mol)**
Cl-	-460.2714632	N.A.	N.A.	1.48	36.7	-74.6	-288823.2	-288908.8
H2O	-76.43312825	N.A.	13.401	2.372	46.493	-2.1	-39552.9	-47962.6
H+	N.A.	N.A.	N.A.	N.A.	N.A.	-265.5	N.A.	-265.5
H3O+ (gas opt)	-76.70705228	N.A.	21.608	2.424	48.433	-110.2	-34683.0	-48235.0
H3O+ (solv opt)	-76.70581672	-0.160348678	22.048	1.776	12.3	1.9	-48210.4	-48212.2
C2H4	-78.59790973	N.A.	32.072	2.502	52.327	N.A.	-49286.4	-49302.0
CuCl2	-1269.510437	-0.042522505	32.871	6.078	27.559	1.9	-796617.6	-796623.9
solv PtCl2(OH)2	-1191.305074	-0.335509376	17.858	5.209	20.857	1.9	-747742.7	-747747.0
solv PtCl2(OH)	-1191.973577	-0.118941504	25.478	5.717	25.985	1.9	-748018.2	-748024.0
solv PtCl2(H2O)2	-1192.491454	-0.048972464	33.615	5.905	27.325	1.9	-748290.9	-748297.2
solv PtCl3(OH)	-1575.727198	-0.317365537	10.184	5.145	21.382	1.9	-988967.6	-988972.1
solv PtCl3(H2O)	-1576.385745	-0.108078923	18.084	5.438	23.599	1.9	-989241.3	-989246.5
1-PdCl4	-1967.726836	-0.3009667	2.466	5.074	21.549	1.9	-1234948.6	-1234953.1
1-PdCl4 (H2O)	-2044.18693	-0.289128439	17.078	7.387	38.663	1.9	-1282903.7	-1282913.3
1-PdCl4 (H3O)	-2044.769237	-0.124749836	24.801	6.956	34.421	1.9	-1283158.6	-1283167.0
2-PdCl3L	-1586.144684	-0.09311243	36.154	5.808	25.282	1.9	-995337.3	-995343.0
2-PdCl3L (H2O)	-1662.596101	-0.090288129	50.48	8.428	46.122	1.9	-1043292.6	-1043304.5
2-PdCl3L (H3O)	-1663.060877	-0.046353089	59.257	7.691	38.709	1.9	-1043548.6	-1043558.3
3-PdCl2LH2O cis	-1202.246372	-0.038846514	51.441	6.36	29.158	1.9	-754387.6	-754394.4
3-PdCl2LH2O cis (H2O)	-1278.700721	-0.037574232	66.746	8.146	43.297	1.9	-802345.5	-802356.5
3-PdCl2LH2O cis (H3O)	-1279.036629	-0.118840025	74.44	8.471	45.284	1.9	-802599.3	-802610.9
4-PdCl2LOH	-1201.738494	-0.09707155	43.716	5.946	25.783	1.9	-754113.6	-754119.4
6-PreBHE1	-1201.717402	-0.112926037	43.399	6.063	30.42	1.9	-754110.5	-754117.7
9-PdCl3(CH2CH2OH)	-1661.944069	-0.299722153	45.683	6.924	34.915	1.9	-1043021.2	-1043029.7
9H-PdCl3(CH2CH2OH2)	-1662.521952	-0.14249668	52.994	6.849	33.881	1.9	-1043277.9	-1043286.1
10-PdCl2(CH2CH2OH)	-1201.722309	-0.114749903	45.406	5.55	25.097	1.9	-754113.2	-754118.8
10-PdCl2(CH2CH2OH) (H2O)	-1278.185324	-0.106611689	60.831	7.134	34.862	1.9	-802072.4	-802080.9
10-PdCl2(CH2CH2OH) (H3O)	-1278.585348	-0.121726245	68.265	7.479	40.571	1.9	-802325.1	-802335.3
TS-ALE1	-1662.566194	-0.095235686	51.435	7.212	34.792	1.9	-1043277.2	-1043285.7
Hydroxypalladation TS	-1201.697034	-0.109246091	43.34	5.579	24.34	1.9	-754095.9	-754101.3
TSInt-H2Oonly	-1202.131802	-0.097663776	53.181	5.222	21.954	1.9	-754352.0	-754356.7
TS-INT	-1278.635007	-0.060109084	65.949	7.224	35.44	1.9	-802320.2	-802328.8
TS-ALE2	-1738.988372	-0.1120983	67.371	8.162	44.105	1.9	-1091226.5	-1091237.8
TS-EXT	-1662.517034	-0.145930788	52.38	7.208	36.743	1.9	-1043277.2	-1043286.3
TS-ISO	-1201.71459	-0.109717736	44.686	5.366	24.512	1.9	-754106.1	-754111.5
Cu-1	-3084.420764	-0.252857719	4.535	8.708	48.984	1.9	-1935648.8	-1935661.5
Cu-2	-2702.79346	-0.089319133	38.077	9.547	54.082	1.9	-1696037.0	-1696051.2
Cu-3	-2318.856225	-0.068900963	53.515	10.039	56.846	1.9	-1455084.0	-1455099.0
Cu-4	-2318.386471	-0.092676314	45.569	9.728	54.403	1.9	-1454812.4	-1454826.7
Cu-5	-2394.827526	-0.115536831	62.89	11.21	67.052	1.9	-1502775.4	-1502793.5
Cu-6	-2318.368906	-0.112397263	45.292	9.316	52.661	1.9	-1454814.4	-1454828.2
Cu-9	-2778.640763	-0.25564166	47.793	10.528	61.738	1.9	-1743725.6	-1743742.1
Cu-9-H	-2855.674914	-0.101941507	70.521	11.725	68.183	1.9	-1791944.9	-1791963.3
Cu-10	-2318.378585	-0.109753348	47.57	9.11	51.122	1.9	-1454816.8	-1454830.1
Cu-TS-ALE1	-2779.206335	-0.0962792	53.472	10.889	63.058	1.9	-1743974.4	-1743991.3
Cu-TS-INT	-2395.245891	-0.095050042	68.306	11	64.806	1.9	-1503019.9	-1503037.3
Cu-TS-EXT	-2779.171801	-0.141675407	54.376	10.947	65.809	1.9	-1743980.3	-1743998.0
Cu-TS-ISO	-2318.365767	-0.113115444	46.306	9.178	52.713	1.9	-1454812.0	-1454825.9
Cu-TS-ALE2	-2855.613871	-0.140395922	70.008	11.897	71.523	1.9	-1791931.0	-1791950.5